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(54) FIBRILLATABLE FILAMENTS AND BULK YARN OF IMPROVED DYEABILITY

(71) We, ALLIED CHEMICAL CORPORATION, a Corporation organized and existing under the laws of the State of New York of 61 Broadway, New York 6, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to blends of incompatible polymers, and to fibrillated filaments obtained readily therefrom and processes for their production.

To avoid the expense of preparing staple yarn, synthetic monofilaments are required that can be mechanically split into numerous fine fibrils, which are desirable for fabrics with a high bulk and good tactile qualities. These splittable monofilaments are generally prepared from mixtures of certain incompatible polymers which are inert and mutually insoluble. For example, mixtures of polyethylene and nylon that will split into fibrils upon mechanical manipulation have been disclosed in British patent 930,074. However, such fibrils have poor dyeability, for polyolefins are difficult to dye and the excellent dyeability of nylon is reduced in proportion to the amount of polyolefin present.

In one aspect the invention comprises a composition containing (a) 5—80% by weight of a graft copolymer having a polyimine backbone wherein the imino nitrogen atoms are separated from each other by an average of no more than five chain atoms and carry polyamide side chains which have 3 to 18 chain atoms, generally 5 to 11 methylene groups, between the amide and

carbonyl groups, and a number average molecular weight of at least 500 but no more than about half the average molecular weight of the backbone, and (b) from 95 to 20% by weight of at least one polyolefin or polyester or a mixture of both.

In another aspect the invention comprises fibrillatable strands obtained from these compositions.

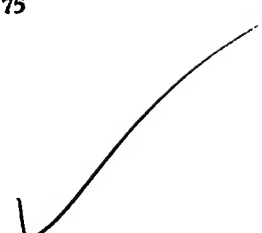
In yet another aspect the invention comprises a method for preparing fibrillated yarn by subjecting the fibrillatable strand to mechanical manipulation to convert it to a yarn with a multifibril structure. Thus fibrillated yarn can be dyed very well by acidic dyes and hence well dyed fabrics made from this yarn are readily obtained.

Suitable polyimine-polyamide graft copolymers are described in U.S. Patent Specification No. 3,442,975. They can be prepared by polymerising a lactam under non-alkaline conditions in admixture with from about 0.1 mol to about 25 mols per 100 mols of lactam, of a polyimine having a molecular weight of at least 20,000, preferably from about 50,000 to about 500,000. A graft copolymer comprising a polycaprolactam side chain on a polyethyleneimine backbone is preferred.

Suitable polyolefins are crystalline polymers or copolymers of alpha-olefins such as polyethylene, polypropylene, polybutene - 1, and poly - 4 - methylpentene - 1, isotactic polypropylene being preferred.

Suitable polyesters can be prepared from aromatic and aliphatic dicarboxylic acids or their esters or acyl halide derivatives, and glycols in known manner. Thus the acid component may be for example oxalic, malonic,

[Price 5s. 0d. (25p)]



- succinic, glutaric, adipic, suberic, azelaic, sebacic, terephthalic or isophthalic acid, *p* - carboxyphenylacetic acid, *p,p'* - diphenyl-dicarboxylic acid, *p,p'* - dicarboxydiphenylsulphone, *p* - carboxyphenoxyacetic acid, *p* - carboxyphenoxypropionic acid, *p* - carboxyphenoxybutyric acid, *p* - carboxyphenoxyvaleric acid, *p* - carboxyphenoxyhexanoic acid, *p,p'* - dicarboxydiphenylmethane, *p,p'* - dicarboxydiphenylethane, *p,p'* - dicarboxydiphenylpropane, *p,p'* - dicarboxydiphenylhexane, *p,p'* - dicarboxydiphenoxyethane, *p,p'* - dicarboxydiphenoxypentane, 3 - alkyl - 4 - (*p* - carboxy - ethoxy) - benzoic acids, condensed ring acids such as 2,6 - naphthalene dicarboxylic acid, 2,7 - naphthalene dicarboxylic acid, or saturated ring acids such as hexahydroterephthalic acid. Mixtures of acids can be used containing up to 30 per cent of a second dicarboxylic acid from the above list.

The glycol component may be for example of the general formula:—



- wherein *n* is an integer from 2 to 10 such as ethylene glycol, butylene glycol 1,5-pentanediol, nonylene glycol; branched-chain aliphatic glycols such as 2,2 - dimethyl - 1,3 - propanediol, 2 - methyl - 1,5 - pentanediol; cycloaliphatic glycols such as 1,4 - cyclohexadimethanol; 1,3 - cyclohexanediol and 1,4 - cyclohexanediol; aromatic glycols such as *p* - xylylene glycol, resorcinol, pyrocatechol, cresorcinol, and alkyl substituted aromatic glycols; and diphenols such as bis(4 - hydroxyphenyl)dimethylmethane, and 4,4 - bis(hydroxycumyl)benzene. Mixtures of these and other suitable glycols well known in the art can also be employed.

- The preferred polyester is polyethylene terephthalate.

- The compositions of the invention comprise 5—80% by weight of the polyimine-polyamide graft copolymer with 95—20% by weight of at least one polyolefin, polyester or a mixture of the two (when more than one polymer is blended with the graft copolymer, their relative proportions are not critical and can vary from about 1 to about 99% by weight of each). If less than about 5% by weight of the graft copolymer is present in the composition, the dyeability, e.g. of polyolefins, will not be substantially improved while if more than 80% by weight is present homogeneous compositions giving substantially non-splittable filaments are obtained. It is generally preferred to use about 10 to 60% by weight of the graft copolymer in the composition for as the proportion increases above 60%, the splittability of the filaments formed therefrom begins to fall off.

Preferred compositions comprise 10—60% of a polyethyleneimine-polycaprolactam

graft copolymer with 90—40% by weight of polyethylene terephthalate, polypropylene or a mixture of the two.

The compositions of the invention can be prepared by heating an appropriate mixture of the polymers so that the mixture is liquid. Temperatures from the melting point of the highest melting polymer to temperatures near the decomposition point of the polymers can be used, temperatures of from about 250°C. to about 320°C. being generally preferred. The polymers can be intimately mixed before melting, or blended in the melt, e.g. by stirring or extrusion. Blending is preferably carried out under a dry inert atmosphere to maintain a low moisture content in the blend.

Alternatively the compositions can be prepared in solution by dissolving the polymers in a suitable solvent and precipitating the mixture, either by evaporating the solvent or by adding to the solution a non-solvent for the polymer mixture.

A fibrillatable strand can be obtained either by forming a sheet or film of the composition and cutting it into strips, or, preferably, by extending the composition as a monofilament. Typically, blending, melting and forming are all accomplished in a single step in an extruder. The strands can be drawn by conventional techniques.

The drawn monofilaments or strips can be fibrillated by suitable well known means. The preferred method is a two-stage technique described in U.S. Patent Specification No. 3,506,535, in which surface area is increased by drawing and the drawn strand passed through a high velocity air stream which splits it into a multitude of fine fibrils.

The invention is illustrated by the following Example, wherein all parts and percentages are by weight. Melt index was determined according to ASTM Test D1238-65T using a 325 gram weight at 235°C. Reduced viscosity was determined as an 0.5% by weight solution in *m*-cresol at 25°C.

EXAMPLE I

Part A: Preparation of the Graft Copolymer

75.5 parts of a 20% aqueous solution of polyethyleneimine having a molecular weight of 200,000, 1600 parts of ϵ -caprolactam and 80 parts of ω -aminocaproic acid were charged to a reaction flask fitted with a reflux condenser, inlet and outlet for nitrogen and a stirrer, and heated at reflux temperature for two hours. The temperature was then raised to 260°C. when the water distilled off. The temperature was maintained at 260—270°C. for 15 hours. The product was cooled, ground and extracted with boiling water to remove any residual monomer or low molecular weight material. The polymer was dried under vacuum.

The product, a graft copolymer containing 1% of polyethyleneimine, had a reduced viscosity of 1.28 and a melt index of 7.3. The product had 0.179 meq of amine end groups and 0.009 meq of carboxyl end groups per kilogram of polymer.

Part B: Preparation of the Blend

40 parts of the graft copolymer as prepared in Part A, 30 parts of polyethylene terephthalate having a reduced viscosity of 0.3 and 30 parts of polypropylene having a reduced viscosity of 2.39 and a molecular weight of 296,000 were blended and extruded in a Reifenhauer extruder Model S-013 having a 1/2 inch diameter screw with a length to diameter ratio of 24:1 at a temperature of 280°C. A monofilament having a diameter of 0.015 inch was collected and drawn at a ratio of 4:1 over a heater maintained at 160°C. The stretched monofilament was slightly crushed by passing between rollers having a clearance of 0.002 inch between them. The crushed monofilament was then passed through an air jet stream having a pressure of 40 psi. The monofilament split into numerous continuous fibrils.

Part C: Dyeing of the Fibre

A sample of the split fibre as formed in Part B was stirred in a scouring solution containing 2% by weight of the fibre of sodium phosphate and 0.5% by weight of the fibre of Triton X-100 (a Registered Trade Mark for a surface active agent of Rohm and Haas Co.) at 160°F. After rinsing the fibre thoroughly with water, they were immersed for one hour in a boiling dye bath containing 0.5% by weight of the fibre of "Kiton" Fast Blue, (C.I. Acid Blue 45) an acid dye obtained from Ciba Co., Inc., 0.6 gram per litre of sodium acetate and 0.5 gram per litre of glacial acetic acid. ("Kiton" is a Registered Trade Mark). The volume of the dye bath was maintained at 40 times that of the fibre.

A fibre control was prepared and dyed as in Parts B and C from a blend containing 40 parts of polycaprolactam having a reduced viscosity of 1.8 in place of the graft copolymer.

The fibre prepared from the blend as in Part B dyed a much deeper shade of blue than the control fibre.

EXAMPLE II

40 parts of the graft copolymer prepared as in Example I, Parts A, and 60 parts of polypropylene as in Example I, Parts B, were blended in an extruder at 260°C. A monofilament was formed having a diameter of 0.02 inch. The monofilament was drawn, crushed, fibrillated and dyed as in Ex-

ample I. A comparison was made to a control fibre prepared in similar manner except substituting polycaprolactam in place of the graft copolymer. The blend of the invention was dyed to a much deeper shade of blue than the control fibre.

EXAMPLE III

50 parts of the graft copolymer prepared as in Example I, Part A, and 50 parts of polyethylene terephthalate having a reduced viscosity of 0.25 were blended and extruded at 280°C. to a monofilament having a diameter of 0.015 inch. The monofilament was drawn to a ratio of 4:1 at 160°C., crushed between rollers and fibrillated as in Example I, Part B. A bulky, multi-fibril yarn was obtained.

WHAT WE CLAIM IS:—

1. A composition comprising (a) 5 to 80 percent by weight of a polyimine-polyamide graft copolymer having a polyimine backbone wherein imino nitrogen atoms are separated from each other on an average by no more than five chain atoms, and carry polyamide side chains which have from 3 to 18 chain atoms between the amide and carbonyl groups and a number average molecular weight of at least 500 but not more than half the average molecular weight of the backbone, and (b) 95 to 20 percent by weight of at least one polyolefin or polyester or a mixture of the two.
2. A composition according to claim 1 wherein the graft copolymer comprises a polycaprolactam side chain on a polyethyleneimine backbone.
3. A composition according to claim 1 or 2, containing 10 to 60 percent by weight of the graft copolymer and from 90 to 40% by weight of at least one polyolefin and/or polyester.
4. A composition according to any one of claims 1—3 containing 10—60% by weight of graft copolymer and 90—40% by weight of polyethylene terephthalate.
5. A composition according to any one of claims 1—3 containing 10—60% by weight of the graft copolymer and 90—40% by weight of polypropylene.
6. A composition according to any one of claims 1—3 containing 10—60% by weight of the graft copolymer, and 90—40% by weight of a mixture of polypropylene and polyethylene terephthalate.
7. A composition according to claim 1 substantially as described herein.
8. A fibrillatable strand obtained from a composition claimed in any one of claims 1—7.
9. A process for preparing fibrillated yarn which comprises subjecting a fibrillatable strand claimed in claim 8 to mechanical

manipulation to convert it to a yarn with a multi-fibril structure.

10. A process for preparing fibrillated yarn substantially as described herein.

5 11. Fibrillated yarn obtained by the process claimed in claim 9 or 10.

12. Dyed fabric containing fibrillated yarn claimed in claim 11.

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